Solvent structure effects in the macroscopic theory of van der Waals forces

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The theory of van der Waals forces is generalized in order to include the effects of solvent structure by explicitly dealing with the spatial correlations between the solvent molecules. This is achieved within the framework of nonlocal dielectric response theory, with the specular reflection approximation to apply the nonlocal response of the structured solvent in the bulk to give the response of such solvent intercalated between the interacting macroscopic surfaces. A closed form expression for the zero-order contribution to the van der Waals free energy is derived for two semi-infinite dielectric regions (characterized by a standard, local dielectric response and fixed dielectric constant), interacting across a layer of a structured solvent described by a nonlocal dielectric response function. The nonlocal character of the latter gives rise to several quantitatively and qualitatively new features of the dispersion interaction; the most important ones are similar in consequences to the effects of spatial variation of the Hamaker coefficient, as seen from the particular case of solvents with an exponentially decaying spatial intersolvent correlations.

I. INTRODUCTION

By and large, the long-range attractive forces between uncharged macroscopic dielectric bodies are due to the fluctuations of the local charge density in these bodies. They are collectively named van der Waals forces and are typically appreciable even at separations greater than 10 nm.

Fluctuations of the local charge density in general give rise to some effective local dielectric polarization. This local polarization then acts as a dipolar field, induces correlated polarization in other polarizable matter and results in a net attraction between the induced and inducing fields. The polarizability of the interacting bodies is therefore essential for the existence of van der Waals forces. Noteworthy, thermodynamically induced fluctuations contribute only to the polarization and orientation forces while the electronic dispersion part of the total van der Waals force is always of quantum mechanical origin.[1]

The ordinary van der Waals force is calculated in the simplest approximation by pairwise summation of the dispersion-, orientation-, and induction-dependent interactions between all molecules. This is the London–Hamaker approach[1,34] which, however, is only of limited value for the description of interactions between macroscopic bodies, because of its inherent, unjustified additivity assumptions.

A more rigorous and powerful method of dealing with electrodynamic fluctuations has been pioneered by Lifshitz[3] and further developed by Dzyaloshinskii, Lifshitz, and Pitaevskii (DLP).[4] These authors have succeeded in resolving the problem of additivity of interactions by analyzing in detail the contributions to the total pressure of the electromagnetic field fluctuations for a nonhomogeneous dielectric system. As a result of this, the total pressure can be expressed as a functional of temporally dispersive, i.e., frequency-dependent dielectric functions of the media involved.

The original, but mathematically rather involved, treatment of DLP has been simplified considerably by Van Kampen, Ninham, Parsegian, and colleagues,[5–9] who have considered van der Waals interactions as a result of the dependence of the eigenfrequencies of various electrodynamic surface modes on the interfacial separation. For the free energy (F) of nonretarded van der Waals interactions between two semi-infinite plan parallel dielectric regions separated by a slab of third dielectric medium with thickness $2a$ they have obtained the result[35]

$$F = \frac{kTS}{4\pi} \sum_{n=0}^{\infty}{}' \int_0^{\infty} Q\,dQ \ln D(\Omega_n, Q, a)$$

$$= -\frac{HS}{12\pi(2a)^2}, \tag{1}$$

where $D(\Omega_n, Q, a)$ is the secular determinant of the electromagnetic modes, kT is the thermal energy, S is the surface area, and Ω_n are the boson frequencies $\Omega_n = 2\pi n(kT/h)$ with h being Planck's constant. The zeros of $D(\Omega, Q, a)$ give the normal mode frequencies of the electromagnetic field as a function of the interfacial separation and of the in-plane (transversal) wave vector Q. The prime in the summation indicates that the first term $n = 0$ is multiplied by $\frac{1}{2}$.

The effective parameter H introduced in Eq. (1) is the Hamaker coefficient and is essentially an empirical parameter in the London–Hamaker approach. Conversely, both the heuristic as well as the DLP theory of van der Waals

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forces provide means for the calculation of this parameter H [cf. Eq. 2(b)] in terms of the dielectric absorption spectra of the interacting dielectric media.

The main advantage of the heuristic approach is that it often provides exactly the same results as the mathematically much more demanding DLP theory. This may also explain the widespread—but erroneous—belief that the two approaches can be used interchangeably. In fact, the simpler heuristic theory is much less general than the DLP approach. It is being inappropriate, e.g., for the description of van der Waals interactions between dielectric bodies immersed in structurable media, including water, at close separations, as we shall show here.

To illustrate this and to introduce a correct procedure for the effective elimination of the problem just mentioned, one can explore the expression giving the free energy [Eq. (1)] of nonretarded van der Waals interactions[35] in the case of two identical, semi-infinite dielectric regions "1" with a relatively low dielectric constant interacting across a layer of material "2" with different dielectric properties and with thickness $2a$. The result is[35]

$$F(a) = \frac{kTS}{2\pi} \sum_{n=0}^{\infty} {}' \left\{ \int_0^{\infty} Q \, dQ \ln[1 - \alpha_{12}^2 \right.$$
$$\left. \times \exp(-4Qa)] \right\}. \qquad (2)$$

The reflection coefficient α_{12} introduced in Eq. (2) is a function of dielectric premittivities ϵ_i:

$$\alpha_{12} = \epsilon_1(i\Omega_n) - \epsilon_2(i\Omega_n)/\epsilon_1(i\Omega_n) + \epsilon_2(i\Omega_n), \qquad (2a)$$

which must be evaluated at imaginary (boson) frequencies ($\Omega_n = n \times 2.5 \times 10^{14} \, \text{s}^{-1}$ at 300 K).

After expansion of the logarithmic term in Eq. (2) and truncation at the lowest order term,[1] the Hamaker coefficient is found to be given by

$$H = \frac{3}{4} \left\{ kT \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^2 + \frac{h}{\pi} \int_{\Omega_1}^{\infty} \left[\frac{\epsilon_1(ix) - \epsilon_2(ix)}{\epsilon_1(ix) + \epsilon_2(ix)} \right]^2 dx \right\} \qquad (2b)$$

with ϵ_i now being identical to the static dielectric constant $\epsilon_i (\Omega = 0)$. The Hamaker coefficient for two hydrocarbon layers interacting across a water filled region evaluated from the approximate expression (2b) agrees to within 95% with the exact result deducible from Eq. (2). It yields a value of $H \simeq 3$–6×10^{-21} J,[1] the measured value being $H \simeq 7 \pm 1 \times 10^{-21}$ J.[20]

The handicap of all common approximations for the calculation of van der Waals interactions is that they account for the dispersion-, orientation-, and induction-dependent interactions, but typically make no allowance for the effects of the spatial correlations between the solvent molecules, i.e., for the solvent structure. This is a severe shortcoming which becomes for most practically relevant media particularly manifest at small interfacial separations.

The reason for this is that at large interfacial separations, the electric field in the intervening region 2 varies only slowly with the transversal coordinate so that the dielectric response in this region is governed by the usual static dielectric constant, for water $\epsilon_2 = \epsilon \simeq 78$–$80$. For smaller interfa-

cial separations, however, the spatial variation of the electric field within the region 2 becomes so rapid that the solvent molecules can no more strictly follow the field's dictate at all places. The dielectric response of the solvent in this case is determined by an effective dielectric constant which is much lower than in the previous case; ultimately, the value of this constant may even become similar to that of the regions 1. To see how the solvent structure influences the van der Waals interactions, it is therefore sufficient to consider the zero-order contribution to Eq. (2) with appropriate dielectric constant values

$$F_0(a) = \frac{kTS}{4\pi} \int_0^{\infty} Q \, dQ \ln \left[1 - \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^2 \right.$$
$$\left. \times \exp(-4Qa) \right]. \qquad (3)$$

If the magnitudes of ϵ_1 and ϵ_2 become comparable, the interfacial attraction gets markedly smaller than that typical of the large interfacial separations, reminiscent of a diminution of the total effective Hamaker coefficient.

In this work we investigate such effects theoretically. We present a detailed study of the contribution to van der Waals attraction from the solvent between two parallel planar, semi-infinite dielectrically homogeneous regions. For this, we adopt the method of nonlocal electrostatics. Firstly, because in our view this is the natural way of implementing the effects of spatial intersolvent correlations into macroscopic theories of van der Waals forces. Whereas classical models of dispersion force are concerned with the time dispersion in the interacting dielectric media, and therefore involve the frequency dependent dielectric permeability $\epsilon(\omega)$, the nonlocal electrostatics deals with the spatial dielectric dispersion in order to allow for the effects of solvent structure, and correspondingly explores the behavior of the wave-vector dependent permittivity $\epsilon(\mathbf{k}, \omega = 0)$. The nonlocal electrostatic treatment also provides means for mathematically—albeit not also conceptually—more straightforward modeling of the solvent structure than, e.g., the theories of liquids.

The macroscopic continuum treatment followed here is thoroughly vindicated by the success of the macroscopic theories in dealing with structural forces in aqueous solutions.[11-14] This approach, however, is as yet not applicable to the analysis of oscillatory forces superimposed on the monotonous component, observed in some systems.[26,27]

II. TEMPORAL DISPERSION IN DIELECTRIC MEDIA

As already noted, the van der Waals force depends on the polarizability of the media involved.

For a dielectric continuum or a structureless solvent the relation between the dielectric displacement vector $\mathbf{D}(\mathbf{r},t)$ and the electric field vector $\mathbf{E}(\mathbf{r},t)$ is

$$\mathbf{D}(\mathbf{r},t) = \epsilon_0 \mathbf{E}(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t),$$

where ϵ_0 is the permittivity of free space.

Normally, however, the induced polarization $\mathbf{P}(\mathbf{r},t)$ is not perfectly synchronous with the electric field, as the former depends on the electric field at all previous times (see, e.g., Refs. 2 and 10). Formally, this can be expressed as

$$\mathbf{P}(\mathbf{r},t) = \epsilon_0 \int_0^\infty f(v)\mathbf{E}(\mathbf{r},t-v)dv$$

with function $f(v)$ describing the time decay of polarization.

If the field fluctuates in time according to

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}(\mathbf{r},\omega)\exp(-i\omega t) ,$$

where ω is frequency, the resulting dielectric displacement vector is given by

$$\mathbf{D}(\mathbf{r},\omega) = \epsilon_0 \mathbf{E}(\mathbf{r},\omega)\left[1 + \int_0^\infty f(v)\exp(-\omega v)dv\right]$$

$$= \epsilon_0 \epsilon(\omega)\mathbf{E}(\mathbf{r},\omega) , \qquad (4)$$

so that Eq. (4) now defines a complex dielectric function of the medium at real frequencies $\epsilon(\omega)$. This and the Kramers–Krönig relations,[2] which express $\epsilon(i\omega)$ through $\epsilon(\omega)$, provide a basis for the evaluation of van der Waals forces from Eqs. (2) and (2a).

Variation with frequency of the function $\epsilon(i\omega)$ is very simple.[2] It takes on only real values; at $\omega = 0$ it is identical to the static dielectric constant and then decreases monotonically towards the value of $\epsilon_\infty \simeq 1$ as the field frequency increases.

If the dielectric decay function $f(v)$ is approximated by a sum of exponential terms of the form

$$f(v) = \sum_{i=1}^N f_i \exp(-\Omega_i v) , \qquad (5)$$

where f_i gives the strength of relaxation, the frequency dependence of the dielectric constant is found to be

$$\epsilon(i\omega) = 1 + \sum_{i=1}^N \frac{(f_i/\Omega_i)}{[1 + (\omega/\Omega_i)^2]} . \qquad (6)$$

If parameter values of Eq. (6) are known or postulated, this result can be used directly to evaluate van der Waals free energy from Eqs. (1) and (2).

III. SPATIAL DISPERSION IN DIELECTRIC MEDIA

In the static case ($\omega = 0$), with the absence of any intersolvent correlations, the electric polarization $\mathbf{P}$ is at every point proportional to the imposed field $\mathbf{E}$:

$$\mathbf{P}_i(\mathbf{r}) = \chi_{ik}\mathbf{E}_k(\mathbf{r}) \qquad (7)$$

the proportionality constants being identical to the elements of the standard dielectric susceptibility tensor. [In Eq. (7) and later, the Einstein convention on the summation of indices is used.]

From macroscopic electrostatics, which implies that the relation between the field and polarization is *local* throughout, the susceptibility tensor of the solvent is deduced to be merely a function of the dielectric constant tensor ϵ_{ik}:

$$\mathbf{P}_i(\mathbf{r}) = \epsilon_0(\epsilon_{ik} - \delta_{ik})\mathbf{E}_k(\mathbf{r}) ,$$

where δ_{ik} is the Kronecker symbol.

For most solvents including water, the previous statements and Eq. (7) are not always strictly valid,[31] however, owing to the correlations between the solvent molecules. A point-like field in a structured medium, e.g., creates a response that is not limited merely to the site of its origin, but due to the intermolecular coupling rather extends over a finite distance of the order of the solvent correlation length ξ. Such a behavior is typical of all structured fluids,[29] irrespective of the detailed molecular mechanism by which the fluid components interact.

Formally this means[11–14,29–31] that in the expression for the electrostatic polarization, the classical local electrostatic relation (7) must be replaced by the *nonlocal* expression

$$\mathbf{P}_i(\mathbf{r}) = \int_V \chi_{ik}(\mathbf{r},\mathbf{r}')\mathbf{E}_k(\mathbf{r}')d^3\mathbf{r}' , \qquad (8)$$

where $\chi_{ik}(\mathbf{r},\mathbf{r}')$ the static dielectric susceptibility tensor depends on the type and strength of intermolecular coupling and integration encompasses the volume in which the medium polarization fluctuations are correlated.

Rewritten in terms of the dielectric displacement vector and of the dielectric parameters of the system, Eq. (8) reads

$$\mathbf{D}_i(\mathbf{r}) = \epsilon_0 \int_V \epsilon_{ik}(\mathbf{r},\mathbf{r}')\mathbf{E}_k(\mathbf{r}')d^3\mathbf{r}' \qquad (9)$$

and implies that in the nonlocal electrostatic approximation the standard static dielectric constant is replaced by an integral operator $\epsilon_{ik}(\mathbf{r},\mathbf{r}',\omega = 0)$. The latter is also called generalized permittivity or the nonlocal dielectric response function. Equation (9) then becomes identical to the classical, local constitutive relation

$$\mathbf{D}(\mathbf{r}) = \epsilon\epsilon_0\mathbf{E}(\mathbf{r})$$

solely if

$$\epsilon_{ik}(\mathbf{r},\mathbf{r}') = \epsilon\delta_{ik}\delta(\mathbf{r}-\mathbf{r}') , \qquad (9a)$$

where $\delta(\mathbf{r})$ is the Dirac delta function.

For three-dimensional, isotropic, translationally invariant media, the kernel of integrals in Eqs. (8) and (9) is diagonal and depends just on the separation $(\mathbf{r} - \mathbf{r}')$. These expressions are therefore in the form of a convolution integral and it is useful to introduce the Fourier transform of the dielectric response function, the so-called spatially dispersive static dielectric function $\epsilon(\mathbf{k}) = \epsilon(\mathbf{k},\omega = 0)$. This corresponds to the supposition that for each plane wave with a wave vector $\mathbf{k}$, the relative permittivity $\epsilon(\mathbf{k})$ attains a different value.

Obviously, for short-wave vectors, the value of $\epsilon(\mathbf{k})$ is identical to the usual static dielectric constant of the medium $\epsilon = \epsilon(\omega = 0)$. With increasing length of $\mathbf{k}$, however, the value of $\epsilon(\mathbf{k})$ decreases until it finally becomes indistinguishable from the high frequency dielectric constant $\epsilon_\infty = \epsilon(\omega \to \infty)$.[31]

Spatial intermolecular correlations coupled to the interfacially induced polarization have been shown, both theoretically[11–14] and experimentally[15–28] to be able to create a strong interfacial repulsive force which, at least for separations less than a few nanometers, exceeds other types of middle- or long-range repulsions. Such force is called solvation force; its ubiquitous importance has been substantiated particularly for aqueous solutions for which the force was named hydration force.

Experiments performed with a variety of hydrated macro- and supramolecular systems, including lipid bilayers and DNA strands have shown that hydration force may give rise to interfacial repulsion as large as 10^9 Pa, decaying ap-

proximately exponentially on a length scale of $0.15 < \xi < 1$ nm. In principle, such hydration force could be due to the dipolar or multipolar interfacial interactions.[51,52] It seems, however, that the largest part of it is a consequence of water structure effects. Correspondingly, it may be modeled within the framework of nonlocal electrostatics because in this approach the correlations between the solvent molecules are inherently dealt with in terms of the dielectric spatial dispersion of the medium.[12–14]

At least for the associated solvents, such as water, the intermolecular coupling effects thus may be taken to die away exponentially on the length scale of the correlation length ξ. Translated into the language of nonlocal electrostatics, this means[13,29] that for structurable media, the following form of the spatially dispersive dielectric function should be used:

$$\epsilon(k) = \epsilon_\infty + \frac{\epsilon - \epsilon_\infty}{(1 + \xi^2 k^2 \epsilon / \epsilon_\infty)} , \qquad (10a)$$

where the parameter values appropriate for water are $\epsilon \simeq 78$, $\epsilon_\infty \simeq 2$–6, and the correlation length is $0.15 < \xi < 1.0$ nm. Formally, Eq. (10a) is identical to the Inkson model dielectric function of solid state physics.[31]

Based on an effective Hamiltonian and measured dielectric dispersion curves, Dogonadze and co-workers[29] have proposed the following extended form of the expression (10a):

$$\epsilon(k) = \sum_{i=1}^{N} \left[\epsilon_i + \frac{\epsilon - \epsilon_i}{(1 + \xi_i^2 k^2 \epsilon / \epsilon_i)} \right] , \qquad (10b)$$

which is remarkably similar to Eq. (6) except in that it pertains to the spatial rather than to the time dispersion in the dielectric medium. Parameter ϵ_i in Eq. (10b) gives the value of the dielectric permittivity just above the ith maximum of the dielectric dynamic absorption spectrum.

IV. FREE ENERGY OF DISPERSION INTERACTION IN THE NONLOCAL ELECTROSTATIC MODEL

Recently Barash and Ginsburg have rederived a result,[32,33] which is as general and accurate as any of the DLP theory despite the fact that it starts with the premises and assumptions used commonly in the heuristic derivations of Eq. (1).

Specifically, these authors have shown that the free energy of electromagnetic fluctuations between two parallel, interacting surfaces can be expressed[33] as

$$F = kT \sum_{n=0}^{\infty} {}' \left[\int_0^\infty \frac{SQdQ}{2\pi} \ln D(\Omega_n, Q, a) \right.$$

$$\left. + \text{Tr} \ln \epsilon_{ik}(\mathbf{r}, \mathbf{r}', i\Omega_n) \right] + \text{const.} \qquad (11)$$

The trace operator Tr stands for the sum (summation over indices and integration over $\mathbf{r}$) of the diagonal elements of the matrix function $\ln \epsilon_{ik}(\mathbf{r}, \mathbf{r}', i\Omega_n)$ and other symbols have their usual meaning. The value of the constant in Eq. (11) is such that it makes the free energy of vacuum fluctuations vanish.[33]

Equation (11) is similar to, but more general than, Eq. (1) because it accounts for the contribution of the surface as

well as bulk longitudinal modes, determined by the zeros the secular determinant and the dielectric function, respetively, to the free energy. The latter contribution, embodie in the trace term, is of paramount importance for the dscription of van der Waals forces within spatially dispersiv media.

The free energy of van der Waals interactions, e.g., c be found from Eq. (11) by calculating the difference

$$V(a) = F(a) - F(a \to \infty) . \qquad (1$$

If the constitutive relation in the space domain is a local on cf. Eq. (4), and the volumes of all dielectric regions are cc stant,[33] the bulk modes are independent of the interfac separation and Eq. (11) reduces to the result of Ninham al.[8] This ceases to be true, however, if the dielectric respon function $\epsilon_{ik}(\mathbf{r}, \mathbf{r}', \omega)$ is an integral operator for which th trace term in Eq. (11) becomes a function of the interfac separation. In the latter case, this trace term must not t omitted, implying that the heuristic approach, which lea to Eq. (1), is inapplicable to the systems with a spatiall nonlocal dielectric response function.

V. SPECULAR REFLECTION MODEL

In order to apply Eq. (11) to the calculation of nonr tarded, zero-order van der Waals forces, solutions to the a propriate Laplace equation must be found and simulti neously the secular determinant and the trace term must k evaluated, for each particular model expression of the diele tric response function.

Our model system consists of two dielectrically unifor half-spaces, separated by a layer of structurable, i.e., "nonlocal" dielectric solvent confined to the region $|z| <$ (Fig. 1).

The bulk structurable solvent is described by an isotroj ic, translationally invariant dielectric function

$$\epsilon_{ik}(\mathbf{r}, \mathbf{r}') = \epsilon(\mathbf{r} - \mathbf{r}') \delta_{ik} .$$

The existence of the boundaries, however, causes the is tropy of the system to break down, at least in the interfaci region, leaving the system translationally invariant only i the transversal, (x, y) directions. In terms of the transvers radius vector $\boldsymbol{\rho} = (x, y)$, the kernel of Eq. (9) then becom

$$\epsilon_{ik}(\mathbf{r}, \mathbf{r}') = \epsilon_{ik}(\boldsymbol{\rho} - \boldsymbol{\rho}'; z, z') .$$

If the spatial dependence of $\epsilon_{ik}(\boldsymbol{\rho} - \boldsymbol{\rho}'; z, z')$ for $|z|, |z'| <$ were known, the solution to the problem would be only matter of mathematical manipulations. Unfortunately, hot ever, this information is, in general, not readily available, that one is confined to using plausible models.

For a point source of electric field at site z', the tot dielectric response $\mathbf{D}$ at some other site z is a sum of th direct response—determined by the Green's function of th bulk dielectric $\epsilon(\boldsymbol{\rho} - \boldsymbol{\rho}'; z - z')$—and of the multiple refle tion terms that arise from the existence of the bounding su faces at $z = \pm a$ (Fig. 1). To describe the latter, the specul reflection approximation may be applied, which can be i terpreted in the following manner.[36,43,44,50]

Imagine that the entire space is filled with a bulk diel tric medium into which fictitious point sources of the electr field are inserted at the points of mirror images, i.e., at z
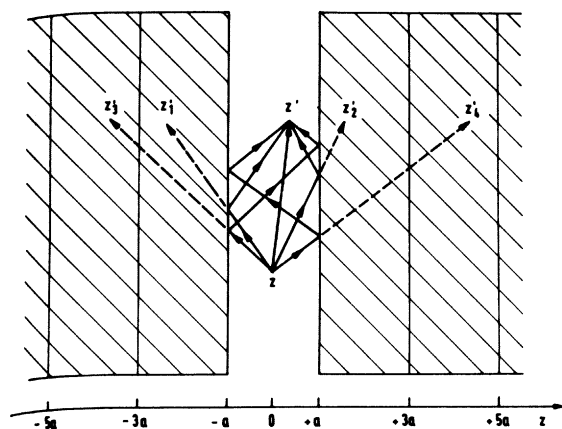
FIG. 1. Schematic representation of the specular reflection approximation for a nonlocal dielectric medium between two plan parallel semi-infinite regions at $z = \pm a$. Every term in the sum [Eq. (13)] corresponds to specular reflections of a beam traveling from z to z'. The first specular reflection corresponds to the path from z to z'_1, the second to the path from z to z'_2, etc.

viz. $z'_{im} = z' \pm 2n2a, 2a - z' \pm 2n2a$, with n being an integer $-\infty < n < \infty$. These hypothetical inputs then contribute to the total response of the system at z, with the bulk Green's function given by $\epsilon(\rho - \rho'; z - z'_{im})$. Owing to the spatial isotropy of this function and of the bulk medium, the specular reflection approximation now implies that the anisotropic dielectric function of the bounded medium is

$$
\epsilon_{zz}(z,z') = \sum_{n=-\infty}^{\infty} \epsilon(2n2a + z - z')
$$
$$
- \sum_{n=-\infty}^{\infty} \epsilon[(2n+1)2a + z + z'],
$$
$$
\epsilon_{ii}(z,z') = \sum_{n=-\infty}^{\infty} \epsilon(2n2a + z - z')
$$
$$
+ \sum_{n=-\infty}^{\infty} \epsilon[(2n+1)2a + z + z'] \quad i = x,y,
$$
(13)

where the explicit dependence of the dielectric functions on $\rho - \rho'$ has been omitted for the sake of simplicity.

Equations (13) embody the modifications in the dielectric response of the medium caused by the proximity of the interfaces. The right-hand side of Eq. (13) depends only on the components of the bulk, isotropic dielectric function of the unbounded dielectric. The left-hand side, however, describes the dielectric response in the region $|z| < a$ and $|z'| < a$, which due to the presence of the interfaces is no longer spatially isotropic. It is clear that as $a \to \infty$, $\epsilon_{ii}(z,z')$ reduces to the bulk form $\epsilon_{ii}(z - z')$.

The constitutive relation Eq. (9) depends on the relation between the real field inside a dielectric medium and the hypothetical field at the sites of the images (which are here denoted by the same letter). The choice of the latter field thereby must be such that its symmetry is identical to that of the dielectric function

$$
E_z(z + 2n2a) = E_z(z),
$$
(14)
$$
E_z(z \pm 2a) = -E_z(-z),
$$
$$
E_i(z + 2n2a) = E_i(z), \quad (i = x,y),
$$
$$
E_i(z \pm 2a) = E_i(-z), \quad (i = x,y).
$$

The postulate of specular reflection is thus equivalent to assuming that the components of the electric field and of the dielectric response function in the direction parallel or perpendicular to the surface are even or odd, respectively, with regard to an inversion about the interfacial plane.

It should be pointed out that the approximations underlaying Eqs. (13) and (14) are all of limited validity,[38] appropriate only for the studies of the static properties of the dielectric media enclosed between two interfaces. In this work this is not a major obstacle since our analysis will be limited to the static $n = 0$ term of Eq. (11) anyhow, this being consistent with the restrictions inherent to the specular reflection model.

Using Eqs. (13) and (14) to express the constitutive relation (9), one gets

$$
D_i(\rho,z) = \epsilon_0 \int_S \int_{-\infty}^{+\infty} \epsilon_{ii}(\rho - \rho', z - z')E_i(\rho',z')d^2\rho'dz',
$$
(15)

a typical convolution-like result suitable for further calculations.

However, owing to the symmetry of the system [cf. Eq. (14)], the electric potential also is a rather simple function of the transversal coordinate z:

$$
\phi(\rho,z) = \frac{1}{a} \sum_{n=0}^{\infty} [\phi_1(\rho,k_n)\cos k_n(z + a)
$$
$$
+ \phi_2(\rho,k_n)\cos k_n(z - a)],
$$
(16)

where $k_n = n(\pi/2a)$.

Expressions (15) and (16) provide a basis for the calculation of the secular determinant for all modes of the electric field in specified geometry, but here only the $n = 0$ term of Eq. (11), which is always nonretarded,[1] will be dealt with.

The secular determinant in the nonretarded limit can be obtained from the Laplace equation[35]

$$
\text{div } \mathbf{D}(\mathbf{r}) = 0
$$
(17)

with boundary conditions requesting that the electric potential and the dielectric displacement are continuous at both interfaces $z = \pm a$.

Surface modes correspond to the plane waves in x,y directions

$$
\phi(\rho,z) = \phi(\mathbf{Q},z)\exp(i\mathbf{Q}\rho).
$$
(18)

If the constitutive relation in the specular reflection model (15) is combined with Eq. (16), the Laplace equation for the region $|z| < a$ is the following:

$$
\epsilon_0 \sum_{i=1}^{2} \left\{ \sum_{n=0}^{\infty}{}' (k_n^2 + Q^2)\epsilon(\mathbf{Q};k_n)\phi_i(\mathbf{Q},k_n) \right.
$$
$$
\left. \times \cos k_n[z - (-1)^i a] \right\} = 0,
$$
(19)

where $\epsilon(\mathbf{Q},k_n)$ is the Fourier transform of the dielectric function of the bulk dielectric medium

$$\epsilon(\mathbf{Q}, k_n) = \int_Q \int_{k_n} \epsilon(\boldsymbol{\rho}, z) \exp\{i[\mathbf{Q}\boldsymbol{\rho} + k_n z]\} \frac{d^2 Q \, dk_n}{(2\pi)^3} .$$

From Eq. (19), the electrostatic potential $\phi_{1,2}(\mathbf{Q}, k_n)$ can be found by simulating the boundary conditions in the form two layers of the induced surface charge with densiti $F_1(\mathbf{Q})$ and $F_2(\mathbf{Q})$ at $z = \pm a$, respectively. The solution the Laplace equation is then

$$\phi(\mathbf{Q}, z) = \frac{1}{a} \sum_{n=0}^{\infty}{}' \frac{[F_1(\mathbf{Q})\cos k_n(z-a) + F_2(\mathbf{Q})\cos k_n(z+a)]}{\epsilon_0(k_n^2 + Q^2)\epsilon(\mathbf{Q}, k_n)} . \tag{2(}$$

For $|z| > a$, the results for the electrostatic potential are of standard form, since in this region the constitutive relation is a local one with $\epsilon_{ik}(\mathbf{r}, \mathbf{r}') = \epsilon_m \delta_{ik}(\mathbf{r} - \mathbf{r}')$. Correspondingly, one has

$$\phi(\mathbf{Q}, z) = (1/\epsilon_0 \epsilon_m) F_3(\mathbf{Q}) e^{Q(z+a)}; \quad z < -a \tag{21}$$

and

$$\phi(\mathbf{Q}, z) = (1/\epsilon_0 \epsilon_m) F_4(\mathbf{Q}) e^{-Q(z-a)}; \quad z > a . \tag{22}$$

The boundary condition for the continuity of the electric potential $\phi(\mathbf{Q}, z)$ at $z = \pm a$ provides further relations from which the induced surface charge densities $F_1(\mathbf{Q})$ and $F_2(\mathbf{Q})$ are deduced

$$F_1(\mathbf{Q})L(\mathbf{Q}; 0) + F_2(\mathbf{Q})L(\mathbf{Q}; -2a) - F_3(\mathbf{Q})/\epsilon_m = 0 , \tag{23a}$$

$$F_1(\mathbf{Q})L(\mathbf{Q}; 2a) + F_2(\mathbf{Q})L(\mathbf{Q}; 0) - F_4(\mathbf{Q})/\epsilon_m = 0 . \tag{23b}$$

Parameters $F_3(\mathbf{Q})$, $F_4(\mathbf{Q})$ are determined by two additional equations derived from the continuity of the dielectric displacement $D_z(\mathbf{Q}; z)$ condition

$$F_1(\mathbf{Q}) + QF_3(\mathbf{Q}) = 0 , \tag{24a}$$

$$F_2(\mathbf{Q}) + QF_4(\mathbf{Q}) = 0 . \tag{24b}$$

In Eqs. (23), we have used

$$L(\mathbf{Q}; z) = \frac{1}{a} \sum_{n=0}^{\infty} \frac{\cos k_n z}{(k_n^2 + Q^2)\epsilon(\mathbf{Q}, k_n)} \tag{25}$$

and

$$\lim_{z \to +0} \frac{1}{a} \sum_{n=0}^{\infty} \frac{k_n \sin k_n z}{(k_n^2 + Q^2)} = 1 . \tag{26}$$

Ultimately, Eqs. (23) and (24) can be combined into a final, condensed form:

$$\sum_k A_{ik}(\mathbf{Q}, a) F_k(\mathbf{Q}) = 0 , \tag{27}$$

where matrix A contains all coefficients of F_i encountered in Eqs. (23) and (24).

The system of linear equations (27) has a nontrivial solution only if its determinant

$$\det A_{ik}(\mathbf{Q}, a) = D(\mathbf{Q}; a) = [(1/\epsilon_m) + QL(\mathbf{Q}; 0)]^2$$
$$- Q^2 L^2(\mathbf{Q}; 2a) \tag{28}$$

is equal to zero. It can be verified easily that in the limit of large separations $a \to \infty$, this result reduces to

$$\det A_{ik}(\mathbf{Q}; a \to \infty) = [(1/\epsilon_m) + QL(\mathbf{Q})]^2 \tag{29}$$

with

$$L(\mathbf{Q}) = \int_0^\infty \frac{dk_z}{(k_z^2 + Q^2)\epsilon(\mathbf{Q}; k_z)} . \tag{30}$$

The eigenfrequencies of the electromagnetic field, i.e., th secular determinant for the electromagnetic modes in a giv en geometry, are obtained for each particular dielectric r sponse if the functional dependence of the latter is incorp rated into Eq. (28) and its zeros are found. In a differer context, Eq. (28) has been investigated by Kliewer an Fuchs.[36]

VI. FREE ENERGY OF DISPERSION INTERACTION IN THE SOLVENTS WITH AN EXPONENTIALLY DECAYIN(RESPONSE FUNCTION

Both characteristic frequencies of the aqueous solu tions, the Debye relaxation frequency, and the relaxatio frequency of ionic plasma are much smaller than even th lowest boson frequency ($\Omega_{n=1}$), being approximatel 10^{-11} and 10^{-12} s^{-1}, respectively. As long as the stati $n = 0$ term in Eq. (11) is treated according to nonlocal ele trostatics, the higher order terms ($n > 1$), therefore, may b dealt with as if they originated from an ordinary dielectri medium characterized by a standard local response,[35] with out any need for nonlocal electrostatic modeling.

We will therefore restrict our calculations to this stati term which will be rewritten as

$$F_0 = \frac{kT}{2} \left[\int_0^\infty \frac{SQ\,dQ}{2\pi} \ln D(Q, a) \right.$$
$$\left. + \mathrm{Tr} \ln \epsilon_{ik}(\mathbf{r}, \mathbf{r}', \omega = 0) \right] + \mathrm{const.} \tag{31}$$

implying that the zero-order free energy is determined solely by the molecular orientation and polarization effects.

For most structurable media, the orientational and po larization effects are associated with the dielectric respons in the static and microwave regions of the absorption spec trum, the effective dielectric constant in the latter region being much smaller than in the former. It has been show that the simplest approximation for the dielectric function o such charge-free dielectric medium (in our case 2) in thi frequency range is given by Eq. (10a), with $\epsilon = 78$, $\epsilon_\infty \simeq 2$ 6, and $\xi \simeq 0.15$–1.0 nm.[29] In contrast to this, the dielectr response within the region 1, that is filled with the nonstru turable material, is determined entirely by a constant diele tric permittivity value, which for hydrocarbons is $\simeq 2$ 6[37,53,54]; noteworthy, the dielectric permittivity in the inte facial (phospholipid headgroup and ester bonds) region likely to be ~ 30.[54]

A formal difficulty with Eq. (31), which has to be over come, arises from the inclusion of the vacuum fluctuation into the constant term. Here one would, strictly speakin

have to deal with infinite frequencies to which the model expression (10a) is not applicable. To retain the consistency, it must be postulated, therefore, that at exceedingly high frequencies the dielectric response of all the media involved in the calculation fulfills the condition $\epsilon(\omega \to \infty) = \epsilon_\infty$, with ϵ_∞ taking the same value as in Eq. (10a). With this amendment, Eq. (31) can be rewritten as

$$F_0 = \frac{kT}{2}\left[\int_0^\infty \frac{SQdQ}{2\pi} \ln\frac{D(Q;a)}{D_\infty(Q;a)}\right.$$
$$\left. + \text{Tr} \ln \epsilon_{ik}(\mathbf{r},\mathbf{r}') - \text{Tr} \ln \epsilon_\infty \right], \qquad (32)$$

where index ∞ now conforms with the definition just given.

The meaning and form of the secular determinant in Eq. (32) have been discussed along with Eq. (28). The trace term $\text{Tr} \ln \epsilon_{ik}(\mathbf{r},\mathbf{r}')$, in Eq. (32), however, has a new and deep meaning that deserves extra attention.

The form of Eq. (19) indicates that the introduction of the specular reflection approximation is formally equivalent to the assumption that the transversal k_z component of the wave vector attains only discrete values. Correspondingly, the trace term in Eq. (32) can be rewritten as

$$\text{Tr} \ln \epsilon_{ik}(\mathbf{r},\mathbf{r}') = \int_0^\infty \frac{SQdQ}{2\pi} \sum_{n=0}^{\infty}{}' \ln \epsilon(\mathbf{Q};k_n) \qquad (33)$$

in analogy with Eq. (19), so that by combining Eqs. (32) and (33), one finally gets

$$F_0 = \frac{kTS}{4\pi}\int_0^\infty Q\,dQ\left[\ln\frac{D(Q;a)}{D_\infty(Q;a)} + \sum_{n=0}^{\infty}{}' \ln\frac{\epsilon(\mathbf{Q};k_n)}{\epsilon_\infty}\right]. (34)$$

Owing to the symmetry of the electric field, Eq. (28) can be written so as to consist only of the products of purely odd and purely even terms with respect to the summation over n. To achieve this, the difference of squares from Eq. (28) is rewritten as a product of the sum and of the difference of these two factors. Correspondingly Eq. (28) can now be written as

$$D(Q;a) = D_{\text{even}}D_{\text{odd}}, \qquad (35)$$

where

$$D_{\text{odd}} = \frac{Q}{a}\sum_{\substack{n=-\infty \\ (\text{odd})}}^{+\infty}\frac{1}{(k_n^2 + Q^2)\epsilon(Q;k_n)} + \frac{1}{\epsilon_m}, \qquad (36)$$

$$D_{\text{even}} = \frac{Q}{a}\sum_{\substack{n=-\infty \\ (\text{even})}}^{+\infty}\frac{1}{(k_n^2 + Q^2)\epsilon(Q;k_n)} + \frac{1}{\epsilon_m}. \qquad (37)$$

By means of the Poisson summation formula (see Appendix A), Eq. (35) can be solved for any reasonable model dielectric function, e.g., such as that given by Eq. (10a). In this latter, special case, the result is

$$D_{\text{odd}} = \left[\frac{1}{\epsilon_m} + \frac{1}{\epsilon}\,cthQa + \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right)\frac{Q}{u}\,cth(ua)\right],$$
$$(38a)$$

$$D_{\text{even}} = \left[\frac{1}{\epsilon_m} + \frac{1}{\epsilon}\,thQa + \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon}\right)\frac{Q}{u}\,th(ua)\right],$$
$$(38b)$$

with $u^2 = Q^2 + \xi^{-2}$.

For vacuum fluctuations, the secular determinant is obtained simply by equating in Eq. (35) the parameter values $\epsilon_m = \epsilon = \epsilon_\infty$, as discussed previously, i.e., by setting

$$D_\infty(Q;a) = \frac{4}{\epsilon_\infty^2}[1 - \exp(-4Qa)]^{-1}. \qquad (39)$$

The last term in Eq. (33) can be evaluated using the logarithmic summation formula (cf. Appendix A). It yields

$$\sum_{n=0}^{\infty}{}' \ln\frac{\epsilon(Q;k_n)}{\epsilon_\infty} = \sum_{n=0}^{\infty}{}' \ln\frac{(1 + u^2/k_n^2)}{(1 + w^2/k_n^2)}$$
$$= \ln\frac{sh(u2a)}{sh(w2a)} \qquad (40)$$

with $w^2 = Q^2 + \epsilon_\infty/\epsilon\xi^2$. An alternative form of Eq. (40) is

$$\sum_{n=0}^{\infty}{}' \ln\frac{\epsilon(Q;k_n)}{\epsilon_\infty} = \ln\frac{[1 - \exp(-4ua)]}{[1 - \exp(-4wa)]}$$
$$+ (u - w)2a. \qquad (41)$$

The first term on the right-hand side of Eq. (41) scales as the surface area (S) and the second as the volume of the structurable region $(S\,2a)$. This is seen from introducing Eq. (41) into Eq. (34) and permits both logarithmic terms in Eq. (34) to be combined into one, area-dependent contribution. (Such rescaling in the free-energy expression then reflects the fact that some of the bulk modes in the specular reflection approximation contain admixed surface modes.[46])

Finally, by using the definition (12) together with Eqs. (29) and (30) in the limit $a \to \infty$, one gets

$$V_0(a) = \frac{kTS}{4\pi}\int_0^\infty Q\,dQ\ln\frac{[1 + \alpha(11)e^{-2(u+Q)a}]^2 - [\alpha(21)e^{-2ua} + \alpha(12)e^{-2Qa}]^2}{(1 - e^{-4wa})} \qquad (42)$$

with

$$\alpha(ik) = \frac{\dfrac{1}{\epsilon_m} + (-1)^i\dfrac{1}{\epsilon} + (-1)^k\left(\dfrac{1}{\epsilon_\infty} - \dfrac{1}{\epsilon}\right)\dfrac{Q}{u}}{\dfrac{1}{\epsilon_m} + \dfrac{1}{\epsilon} + \left(\dfrac{1}{\epsilon_\infty} - \dfrac{1}{\epsilon}\right)\dfrac{Q}{u}}, \quad i,k = 1,2. \qquad (43)$$

The volume term now reads

$$\left\{-\frac{kTV}{4\pi}\frac{\xi^3}{3}[1 - (\epsilon_\infty/\epsilon)^{1/3}]\right\}_\infty^a \qquad (44)$$

and the result should be taken at the indicated limits. This term attains zero value when the volume of the dielectric region 2, enclosed by the two surfaces is constant, but it is per

se insensitive to the existence of the dielectric discontinuities. Correspondingly, expression (44) has nothing to do with van der Waals interactions. It represents merely a contribution to the free energy from the bulk dielectric medium. This aspect is clarified further in Appendix B.

VII. EXAMPLES AND DISCUSSION

The main implications of our results can best be illustrated by showing how the spatial dielectric dispersion, i.e., the solvent structure effects, influence the van der Waals force between two semi-infinite hydrocarbon half-spaces (i.e., very thick layers) interacting across a region of water of thickness $2a$, if the results are calculated within the zero-order approximation.

Hydrocarbon subphase is supposed to be dielectrically homogeneous, characterized by an effective dielectric constant $\epsilon_m = 2\text{--}6$.[37] For the aqueous subphase, which includes hydrated lipid headgroups, the validity of Eq. (10a) may be assumed, corresponding to Eq. (10b) with only the lowest $n = 1$ mode being considered. In this work, we have chosen the parameter values to be $\epsilon = 80$, $\epsilon_\infty = 2\text{--}6$, and $\xi = 0.3$ or 1.0 nm.[12–14,15–28]

Equation (42) suggests that for small interfacial separations, the only significant contribution to the integral over the magnitude of the wave vector Q comes from the region of large Q values of the integrand giving

$$V_0(a \to 0) = \frac{kTS}{4\pi(2a)^2} \int_0^\infty x \, dx \ln\left[1 - \left(\frac{\epsilon_m - \epsilon_\infty}{\epsilon_m + \epsilon_\infty}\right)^2 \times \exp(-2x)\right], \tag{45}$$

where we have $x = Q \, 2a$. Conversely, for large interfacial separations, the major part of the interaction free energy stems from the small wavelength values of the integrand, yielding

$$V_0(a \to \infty) = \frac{kTS}{4\pi(2a)^2} \int_0^\infty x \, dx \ln\left[1 - \left(\frac{\epsilon_m - \epsilon}{\epsilon_m + \epsilon}\right)^2 \times \exp(-2x)\right]. \tag{46}$$

Similar expressions could have been obtained from Eq. (3) with $\epsilon_1 = \epsilon_m$, if values $\epsilon_2 = \epsilon$ and $\epsilon_2 = \epsilon_\infty$ were used for $a \to \infty$ and $a \to 0$, respectively.

Equations (42) and (45) obviously represent only the two limiting cases. In order to study the entire functional dependence on the interlipid water layer thickness $2a$ of the zero-order van der Waals interaction, the complete integral expression (42) must be evaluated numerically.

The insert to Fig. 2 shows the result of one such calculation. It presents the ratio of the effective value of the Hamaker coefficient, evaluated for the cases of intervening media 2 with a local $\xi = 0$ or nonlocal $\xi > 0$ dielectric response, respectively. The relative Hamaker coefficient $H(\xi \neq 0)/H(\xi = 0)$ is seen to vary strongly with the interfacial separation $2a$, attaining in our case a limiting value of 0.27 for closely opposed surfaces; this is due to the fact that the values of the long wavelength dielectric constant of the water-
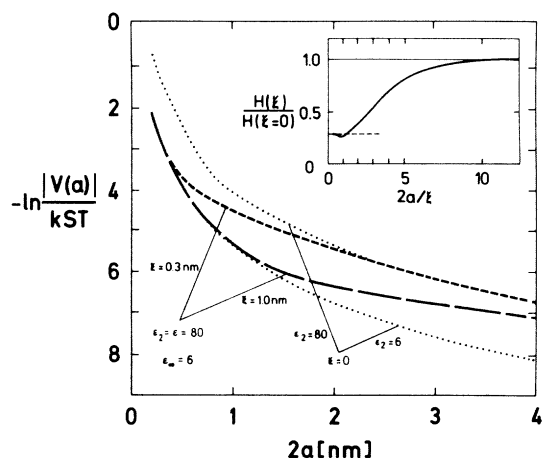

FIG. 2. Logarithm of the leading, zero-order contribution to the van der Waals free energy of interaction between two semi-infinite regions [cf. Eq. (42)], as a function of the interfacial separation $2a$. Dotted curves correspond to the results of a standard evaluation of van der Waals force (local approximation with $\xi = 0$ and $\epsilon_1 = 2$) and were obtained from Eq. (3) with $\epsilon_2 = 80$ and $\epsilon_2 = 6$ for the upper and lower curves, respectively. Dashed curves refer to the situation encountered with structurable solvents. They result from numerically solving Eq. (42) using $\epsilon_m = 2$, $\epsilon = 80$, $\epsilon_\infty = 6$ with $\xi = 0.3$ and 1.0 nm for the upper (- - -) and lower (- - -) curves, respectively. Transition between the regimes corresponding to the high (upper dashed curve) and low (lower dashed curve) effective dielectric constants is clearly seen, the range of transition depending on the choice of the correlation length ξ. The insert shows the ratio of the relative effective Hamaker constants evaluated for the cases of a structurable and simple, structureless media—$H(\xi \neq 0)$ and $H(\xi = 0)$—respectively, as a function of the dimensionless separation $2a/\xi$.

filled $\epsilon_\infty = 6$ and of the hydrocarbon regions $\epsilon_m = 2$ are relatively similar.

Both limiting expressions (45) and (46) can be combined into a simpler phenomenological approximation

$$V_0(a \to \infty) = \frac{kTS}{4\pi(2a)^2} \int_0^\infty x \, dx$$
$$\times \ln\left\{1 - \left[\frac{\epsilon_m - \epsilon_{\text{eff}}(a)}{\epsilon_m + \epsilon_{\text{eff}}(a)}\right]^2 \times \exp(-2x)\right\}, \tag{47}$$

where the effective dielectric constant profile $\epsilon_{\text{eff}}(a)$ has been introduced as

$$\epsilon_{\text{eff}}(a) = \epsilon[1 + (\epsilon/\epsilon_\infty - 1)\exp(-2a/\xi)]^{-1}. \tag{48}$$

Albeit purely phenomenological, this result describes correctly the variation of the effective Hamaker coefficient for any values of the interfacial separation, provided that the validity of Eq. (10) is granted.

The precise value of the ratio $H(\xi \neq 0)/H(\xi = 0)$ is very sensitive to the choice of parameters ϵ, ϵ_∞, ϵ_m, and ξ. Figure 3 illustrates this. For a special case of identical values of the high-frequency dielectric constant of water and of the static dielectric constant of hydrocarbons $\epsilon_\infty = \epsilon_m$, it shows that the calculated van der Waals interaction is rather different if different values of the correlation length ξ are used. This contradicts the classical result [Eq. (3)], which pre-
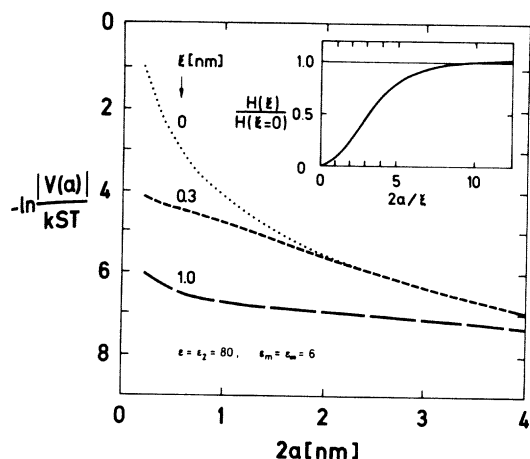
FIG. 3. Logarithmic plot of the zero-order contribution to the van der Waals attraction between two dielectric bodies whose dielectric constants are equal to that of the intervening solvent in the high frequency range $\epsilon_m = \epsilon_\infty = 6$. The uppermost curve pertains to the local model [Eq. (3)] $\xi = 0$ with $\epsilon_2 = 80$ and $\epsilon_1 = \epsilon = 6$, and the two dashed curves illustrate the behavior typical of systems in which the solvent is structured and characterized by a nonlocal dielectric response. The range of the solvent structure effects is seen to be related to the correlation length, which has been taken to be $\xi = 0.3$ and 1.0 nm for the upper and lower curves, respectively. The insert illustrates the variation of the normalized Hamaker coefficient as a function of the dimensionless interfacial separation.

dicts the zero-order van der Waals interaction in such a situation which always vanishes.

Moreover, our results for the case $\epsilon_\infty = \epsilon_m = 6$ suggest (Fig. 3) that the spatial dependence of the zero-order dispersion interaction across structurable solvents does not obey the classical, simple inverse second-power law at short distances; therefore, it can also not be represented by an expression of the form similar to Eq. (47). Careful examination of the free-energy difference in the limit $a \to 0$ for $\epsilon_\infty = \epsilon_m = 6$ rather suggests that for structurable solvents the following lowest order approximation for the interfacial attraction of van der Waals type is appropriate:

$$V_0 = - \frac{kTS}{4\pi\xi^2} \frac{(1 - \epsilon_\infty/\epsilon)^2}{(1 + \epsilon_\infty/\epsilon)}$$

$$\times \frac{1}{8}\left\{ 1 - (4\beta)^2[C - \ln(4\beta)] - \frac{\pi}{2} 4\beta \right\}, \quad (49)$$

where C is the Euler constant ($C \simeq 0.5772$) and

$$\beta^2 = [1 + (\epsilon_\infty/\epsilon)]\tfrac{1}{4}a^2/\xi^2 . \quad (50)$$

Expression Eq. (49) was obtained from Eq. (42) in the specified limit, where all the integrations over Q can be evaluated explicitly.

This conclusion is vindicated by insert to Fig. 3. Here, the ratio of the effective Hamaker coefficient evaluated for $\xi = 0$ and $\xi > 0$, respectively, is shown to vary, albeit not very steeply, with the interfacial separation as the latter approaches zero.

Our model, which accounts for the solvent structure in terms of the corresponding spatial dielectric dispersion, thus yields results which for closely opposed surfaces differ qualitatively from those of the classical van der Waals force the-

ory. This is a general truth that has nothing to do with our particular choice of the dispersion function (10a): It can even be shown that different forms of $\epsilon(k)$ give qualitatively similar results for the variation of the ratio $H(\xi \neq 0)/H(\xi = 0)$ with the interfacial separation.

This indicates rather unambiguously that structuring of the solvent leads to a reduction of the dispersive force between two charge-free media separated by an ion-free solvent.

In the nonlocal electrostatic approximation used in this work, such a diminution of interfacial van der Waals attraction can be shown to originate from an admixture of the bulk modes to the surface modes, as a result of the nonlocal dielectric response within the structurable region.[46] This is tantamount to saying that the fluctuations of the induced surface charge in the dielectrically inhomogeneous media become volume-charge distributions, cease to be bound to the very surface, and begin to penetrate the solvent, owing to the intrasolvent coupling. Interestingly, similar conclusions have also been reached by other authors. Mitchell and co-workers,[41] e.g., have made the same observation based on an entirely different model, stemming from the theory of liquids.

As a caveat it should be noted that the consequences of the nonlocal dielectric response and of the local dielectric inhomogeneities are by no means the same.[39] The former are associated with the *solvent* structure and have been dealt with *in extenso* in the present work. The latter that are the topics of several articles by Parsegian and co-workers[40,42] and arise e.g., when the chemical composition or properties of one of the (semi-infinite) interacting bodies vary with separation. The latter local dielectric inhomogeneities cause the interaction free energy to exceed[40,42] (rather than become smaller than) that of the comparable homogeneous system, since the local inhomogeneities mimic the effect of a diminished effective interfacial separation.

Last, but not least, we wish to stress the correlation between the meaning of our present results, which pertain to the *attractive* interfacial force and imply a negative contribution from the solvent effects, and the results of numerous investigations of the interfacial *repulsive* solvation force. Albeit in principle, different in sign, the former may contribute to the latter and, as far as this work is concerned, indeed represents the other side of the same coin—in both instances one is encountering the consequences of the solvent's incapability to respond to an imposed field locally.

What remains to be resolved is the question of the relation between the results of this work and the experimental work on interfacial van der Waals attraction. Little doubt exists that, at least for aqueous solvents, the dielectric response may be adequately, albeit phenomenologically, described by expressions similar to Eq. (10). In consequence, the solvent effect must be concluded to reduce the standard van der Waals attraction by an amount which depends on the interfacial separation and solvent parameter values. Unfortunately, however, neither are as yet properly established, so that detailed quantitative conclusions about the effects studied in this work are to date impossible. Further difficulty may arise from the fact that the nonstandard contributions

to van der Waals forces, e.g., such that are caused by the correlation effects, probably become greater rather than smaller due to the solvent structure effects.

Nevertheless, our present calculation should be considered useful and informative because of at least two reasons. Firstly, it points to one, doubtlessly existent, consequence of the solvation phenomena in the realm of van der Waals forces. And secondly, it represents a further step towards a consistent generalization of the theory of dispersion forces in a way which would simultaneously account for temporal as well as for spatial dispersion within (and between) interacting bodies. Our next contribution will deal with the implementation of the effects of the fluctuations in ionic distributions into the present model.

In summary, we have shown how the effects of solvent structure can be accounted for within the framework of a generalized electrodynamic theory of van der Waals interactions, by allowing for the nonlocal dielectric response of the medium. We have found that these effectively diminish the dispersive attraction between interacting noncharged bodies if the interfacial separations become comparable to the solvent structure correlation length. We have derived an exact zero-order expression for the calculation of such interactions and have proposed simple phenomenological approximations that can be implemented into standard expressions for the interaction free energy. Work dealing with van der Waals attraction between dielectrics immersed in a structurable electrolyte solution is in progress.

ACKNOWLEDGMENTS

APPENDIX A

We use the Poisson summation formula[45] in the form

$$\frac{1}{a} \sum_{n=0}^{\infty} {}' \frac{\cos k_n z}{(k_n^2 + Q^2)} = \frac{1}{Q} \frac{ch Q(|z| - 2a)}{sh(Q 2a)}, \quad |z| < 2a .$$
(A1)

The related logarithmic summation formula is

$$\sum_{n=1}^{\infty} \ln\left(1 + \frac{Q^2}{k_n^2}\right) = \ln\frac{sh(Q 2a)}{Q 2a} .$$
(A2)

It is important to notice that all summations over the vector component k_n in Eqs. (34) and (25) reduce to different variants of the above two expressions, provided that the dielectric response function is of the form of Eq. (10a).

APPENDIX B

Calculations outlined in the text are based on using Eq. (10a) as a definition of the dielectric response function in the structurable part of the dielectric medium. Similar derivations, however, can also be repeated for media to which the simple Debye response function applies:

$$\epsilon(k) = \epsilon(1 + \kappa^2/k^2) .$$
(B1)

Here κ is the inverse Debye screening length.

If, say, Eq. (B1) is used instead of Eq. (10) throughout

the calculation, this results in the following zero-order van der Waals interaction free energy expression:

$$V_0(a) = \frac{kTS}{4\pi} \int_0^\infty Q\, dQ \ln\left[1 - \left(\frac{\epsilon u - \epsilon_m Q}{\epsilon u + \epsilon_m Q} \right)^2 \right.$$
$$\left. \times \exp(-4ua) \right] - \left[\frac{kTV}{4\pi} \frac{\kappa^3}{3} \right]_\infty^a$$
(B2)

with $u^2 = Q^2 + \kappa^2$.

The first term in Eq. (B2) describes van der Waals interactions experienced by two semi-infinite bodies immersed in an ionic solution.[35] The second describes the standard Debye–Hückel, electrostatic contribution to the free energy of such a system.[47] It is worth noting that a similar expression for the free energy of screened van der Waals interactions is also obtained, if the more common approach,[9,35,48,49] based on the linearized Poisson–Boltzmann equation, is used instead of the specular reflection model.

The total free energy of an electrolyte solution as given by Eq. (B2) thus consists of a surface (van der Waals) term and of a bulk (Debye–Hückel) term, the latter being well known from the theory of ionic solutions. By similar logic, the volume term encountered in Eq. (44) can be interpreted as a contribution to the bulk free energy of the dielectric medium described by the dielectric function given by Eq. (10a).

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